Introduction to the Basics of UV/EB Chemistry and Formulations

SUNY ESF
Radiation Curing Program
RadTech NA

Dr. Mike J. Idacavage
Colorado Photopolymer Solutions
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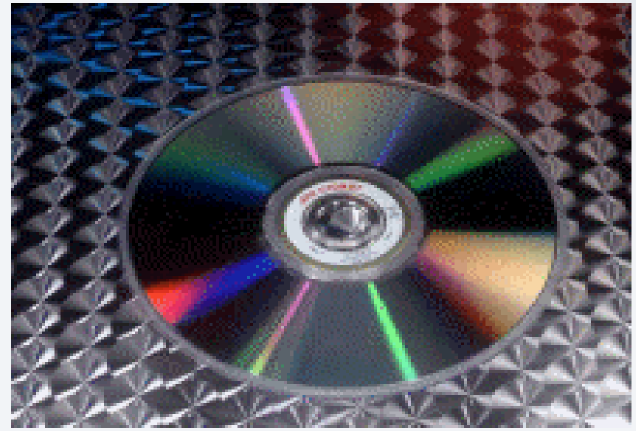
Agenda

- Introduction to UV/EB Curing
- Basic Formulation strategy
- Oligomers
- Monomers
- Photoinitiators
- Cationic Cure
- Electron Beam
- Basics in Action – 3D Printing

Energy Curable Industrial Coatings

Energy Curable Graphic Arts Applications



What is Energy Curing?

- Using UV energy, visible light, or low energy electrons as opposed to thermal, evaporative, or oxidative (air-dry) cure to form a coating, film or ink

- Types of energy used for energy curing:
  - Ultra Violet (UV): 200 – 400 nm
  - Visible light: typically 380 - 450 nm
  - Electron beam: low energy electrons

Note that the terms “radiation curable or “UV/EB curable” may be used interchangeably.

Why Use Energy Curing?

- Productivity, Productivity, Productivity
  - Seconds to cure vs. minutes or hours
- Lower Overall Cost (per cured part)
  - 100% solids, cure speed, recycling of coating, etc
- Single component formulas
  - Eliminates mixing errors found in 2 component systems
- Regulatory Concerns (VOC emission)
  - Avoid solvent use in most cases
- Smaller equipment footprint
  - Less floor space needed
- Energy costs
- Did I mention Productivity?

Areas of Strength for UV/EB Curable

UV/EB Curables can generate a high crosslink density network that results in a coating with high gloss and hardness, scratch and stain resistance and fast cure. UV/EB Curing also works best with flat substrates.

- Examples:
  - Scratch Resistant Coatings (plastic, paper up-grade)
  - Over Print Varnishes (OPV)
  - Printing Inks (Litho, Flexo, Screen)
  - Wood Coatings
  - Electronic & Fiber Optic Coatings
  - Photopolymer Plates

Areas for Improvement

- Adhesion to some metals, esp. during post-forming
- Adhesion to some plastics
- Tear resistance
- Low gloss in 100 % solid systems
- Low film weight for 100% solids
- Overall cure of 3-D parts

UV/EB CURING

TYPES OF RADIATION USED

- UV - ultraviolet photons
- EB - low energy electrons

UV/EB CURING CHEMISTRY

- **Free Radical**
  - Polymerization through double bonds
  - (Meth)Acrylate double bonds most common functionality

- **Cationic**
  - Polymerization through epoxy groups
  - Cycloaliphatic epoxies most commonly used

UV/EB CURING CHEMISTRY

- **Free Radical Curing - UV**
  - Photoinitiator absorbs UV light and generates free radicals
  - Free radicals react with double bonds causing chain reaction and polymerization

- **Cationic Curing - UV**
  - Photoinitiator absorbs UV light and generates a Lewis acid
  - Acid reacts with epoxy groups resulting in polymerization

UV/EB CURING CHEMISTRY

- **Free Radical Curing - EB**
  - Electrons open double bonds initiating polymerization - no photoinitiator required

- **Cationic Curing - EB**
  - Electrons decompose photoinitiator to form acid - photoinitiator is required for polymerization

UV CURING

- (Meth)Acrylated Resin(s)
  basic coating properties
- Monofunctional Monomer(s)
  viscosity reduction, flexibility
- Multifunctional Monomer(s)
  viscosity reduction, crosslinking
- Additives
  performance fine tuning
- Photoinitiator Package
  free radical generation

UV
Light

CURED PRODUCT

EB CURING

- Acrylated Resin(s)
  basic coating properties
- Monofunctional Monomer(s)
  viscosity reduction, flexibility
- Multifunctional Monomer(s)
  viscosity reduction, crosslinking
- Additives
  performance fine tuning

Electrons

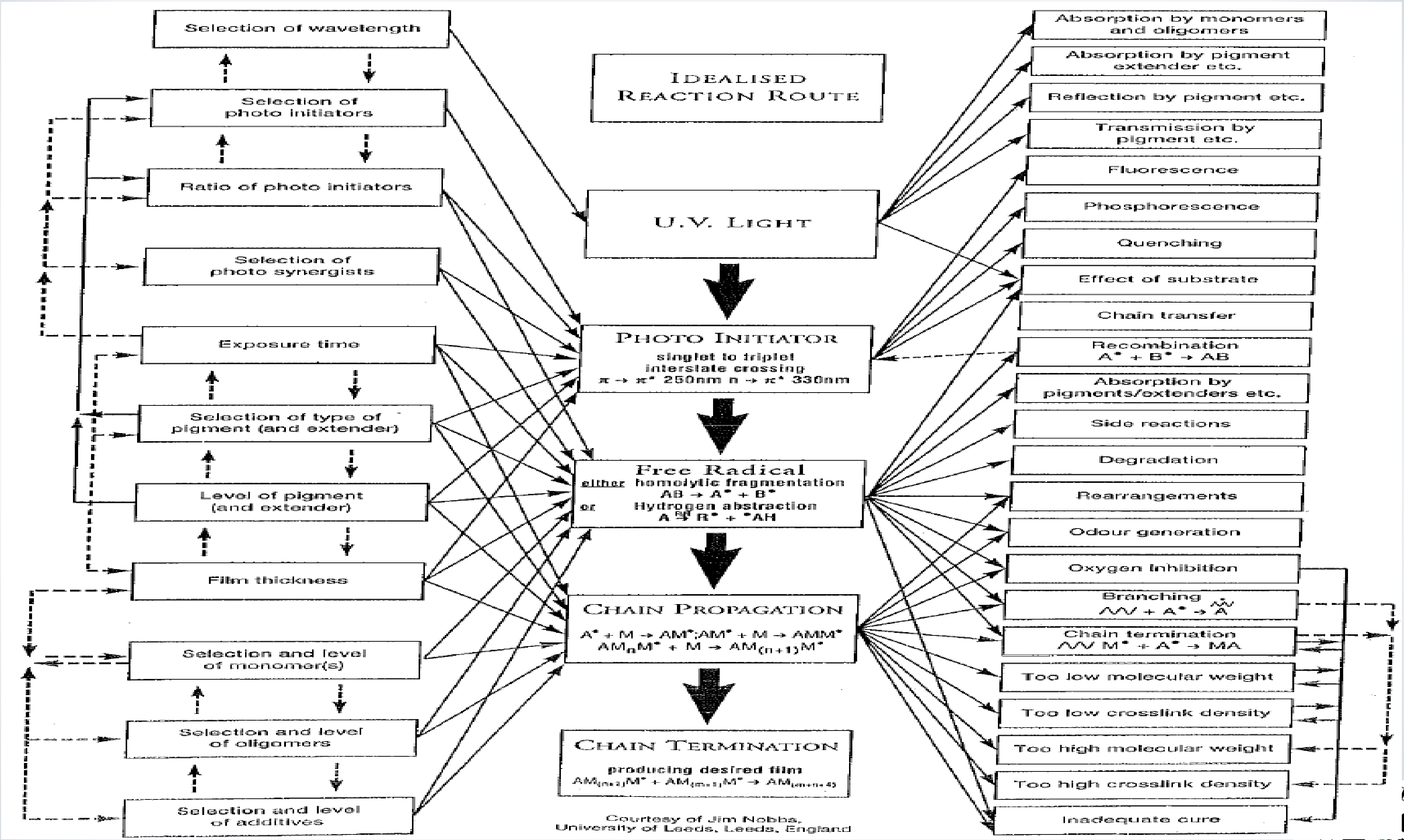
CURED PRODUCT

Formulating for properties

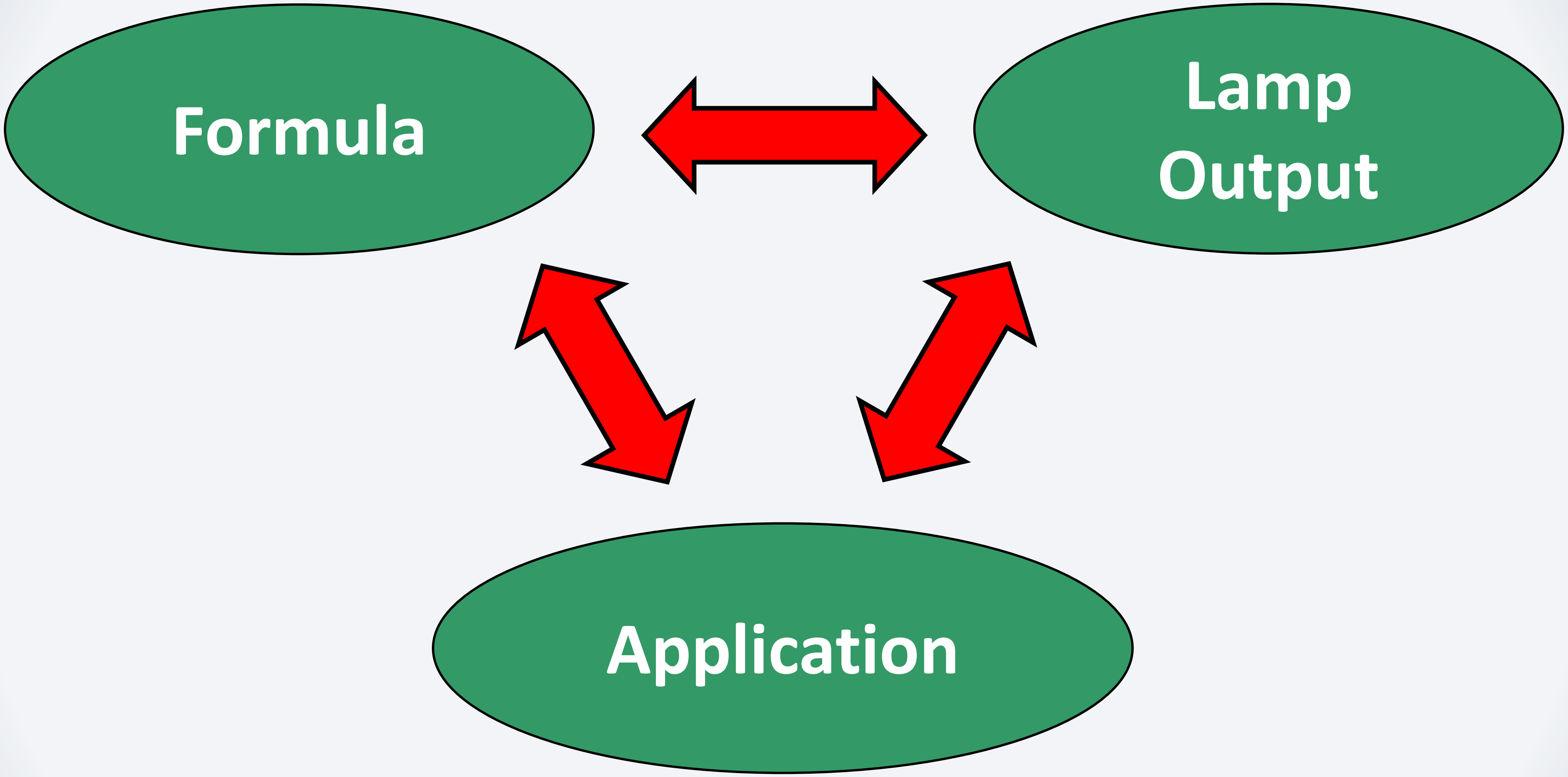
Some desirable properties for coatings:

- Adhesion
- Cure speed
- SARC (scratch & abrasion resistant coatings)
- Weatherability
- Flexibility
- Pigmented systems

Everything You Always Wanted to Know About UV/EB Formulating

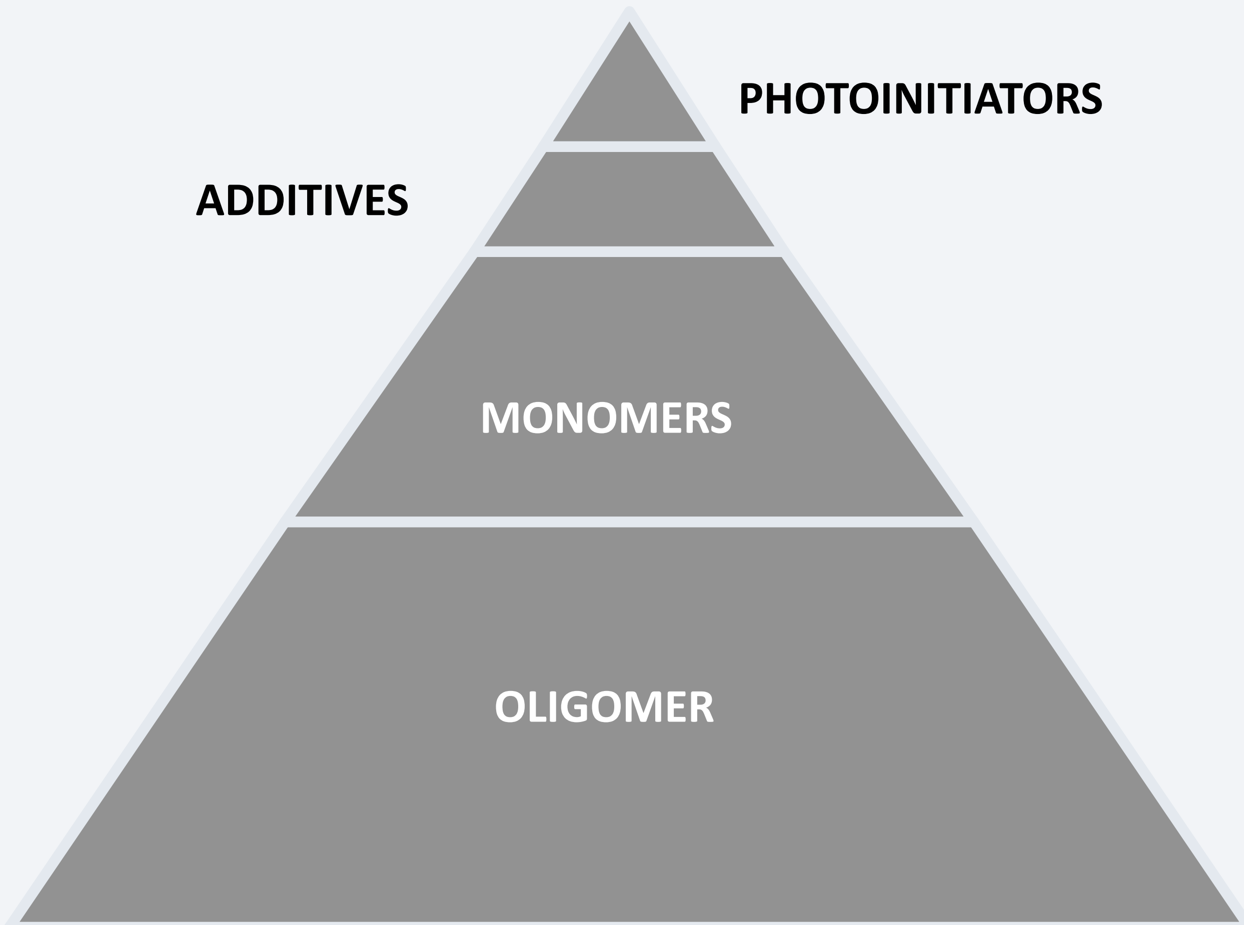


Formulation of EC Products

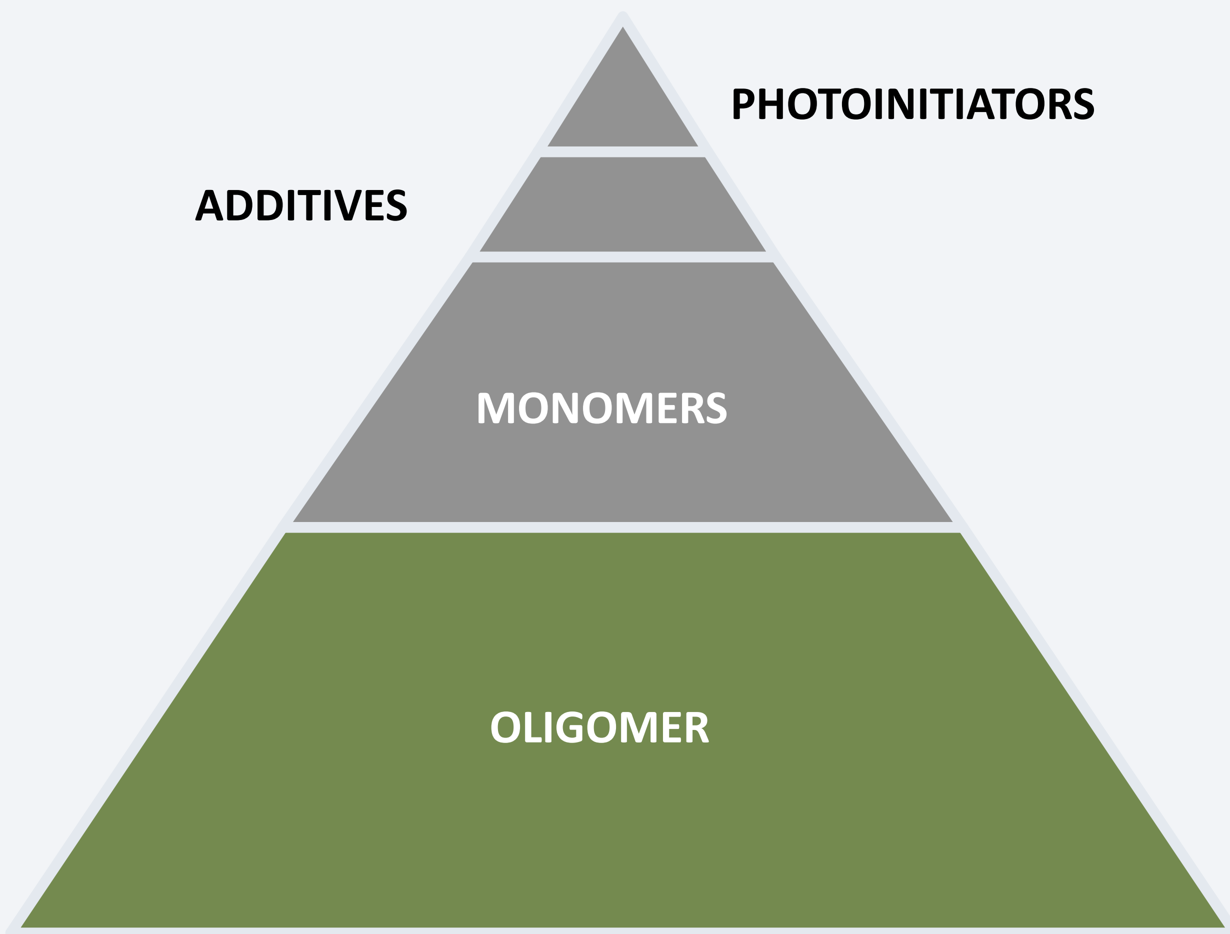


All three aspects are interrelated

FORMULATING A UV CURABLE SYSTEM



FORMULATING A UV CURABLE SYSTEM

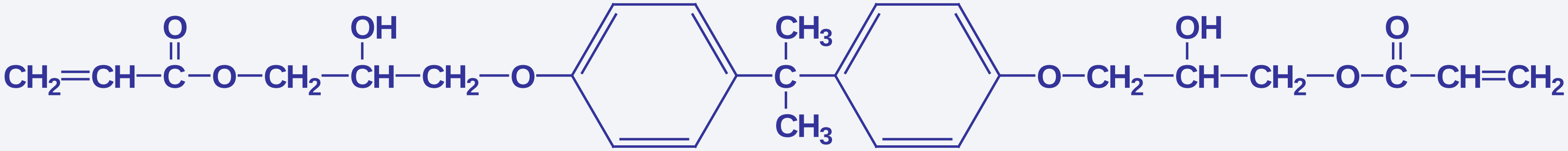


OLIGOMER TYPES

(Meth)Acrylated	**Characteristics**
Epoxies	fast curing, hard, solvent resistant, lower cost
Aliphatic Urethanes	flexible, tough, non-yellowing, best weathering properties
Aromatic Urethane	flexible, tough, lower cost than aliphatic urethanes
Polyesters	low viscosity, good wetting properties
Acrylics	good weathering properties, low Tg
Specialty Resins	adhesion, special applications

OLIGOMERS

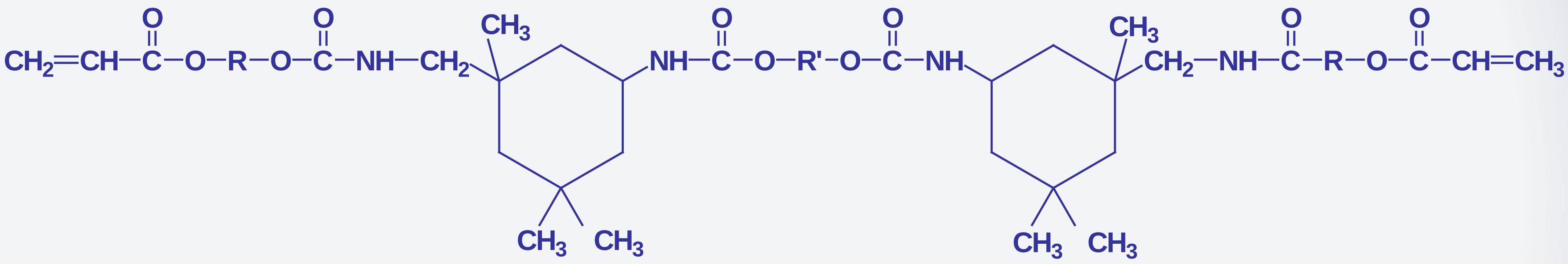
Epoxy Acrylate



bisphenol A diglycidyl ether diacrylate

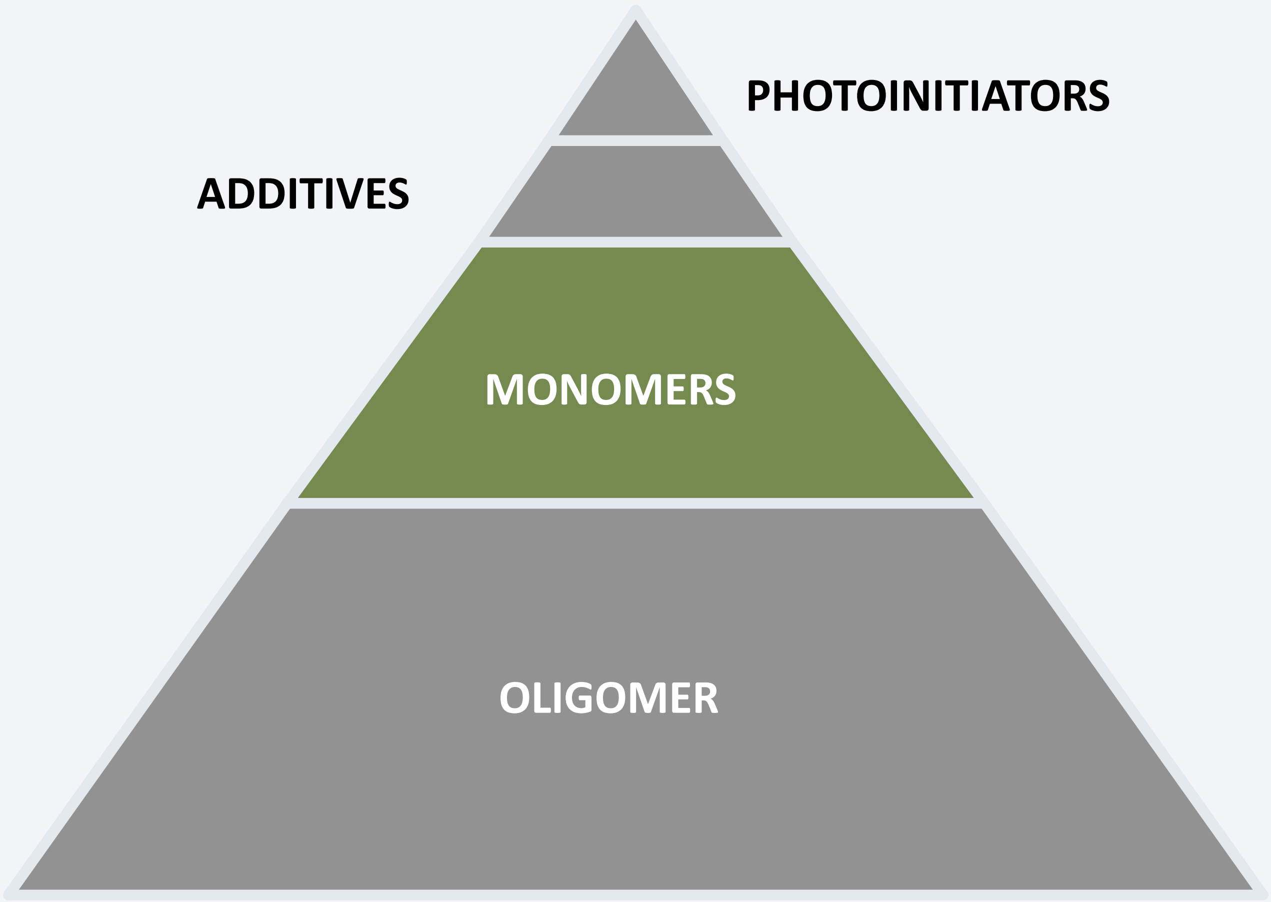
OLIGOMERS

Urethane Acrylate



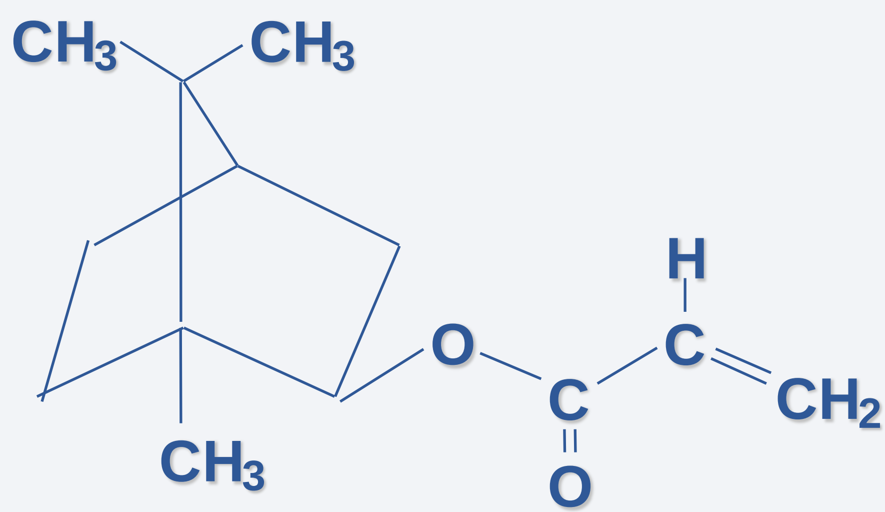
aliphatic urethane diacrylate

FORMULATING A UV CURABLE SYSTEM



MONOMERS

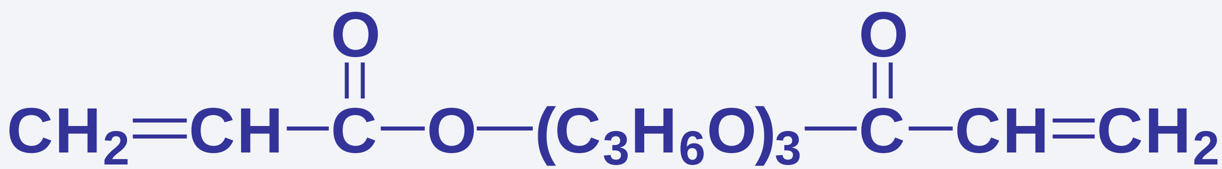
Monofunctional Monomer



IBOA
isobornyl acrylate

MONOMERS

Difunctional Monomer

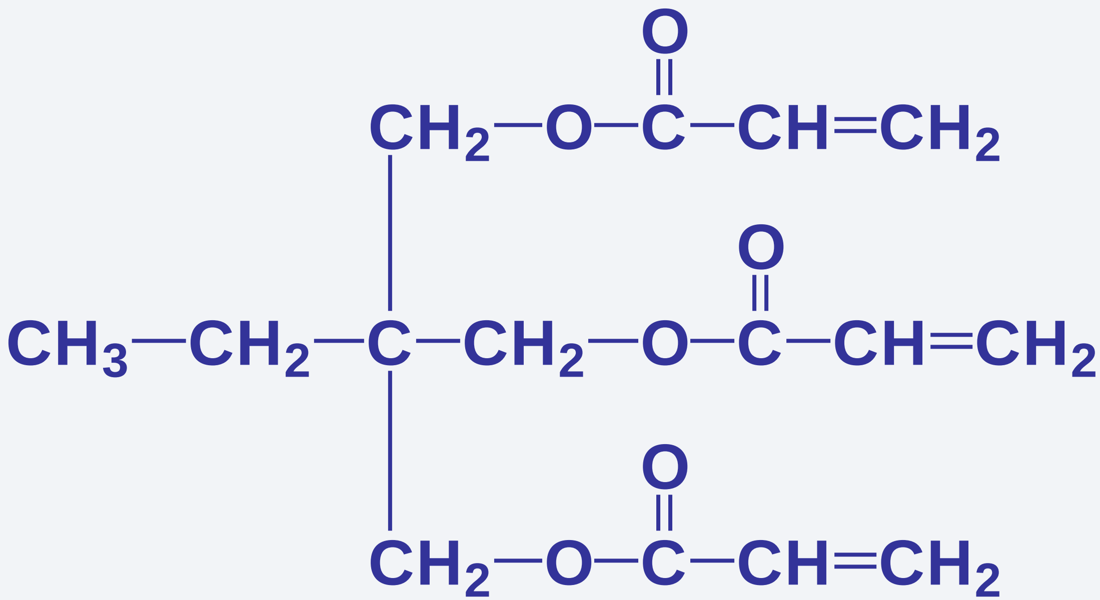


TRPGDA

tripropylene glycol diacrylate

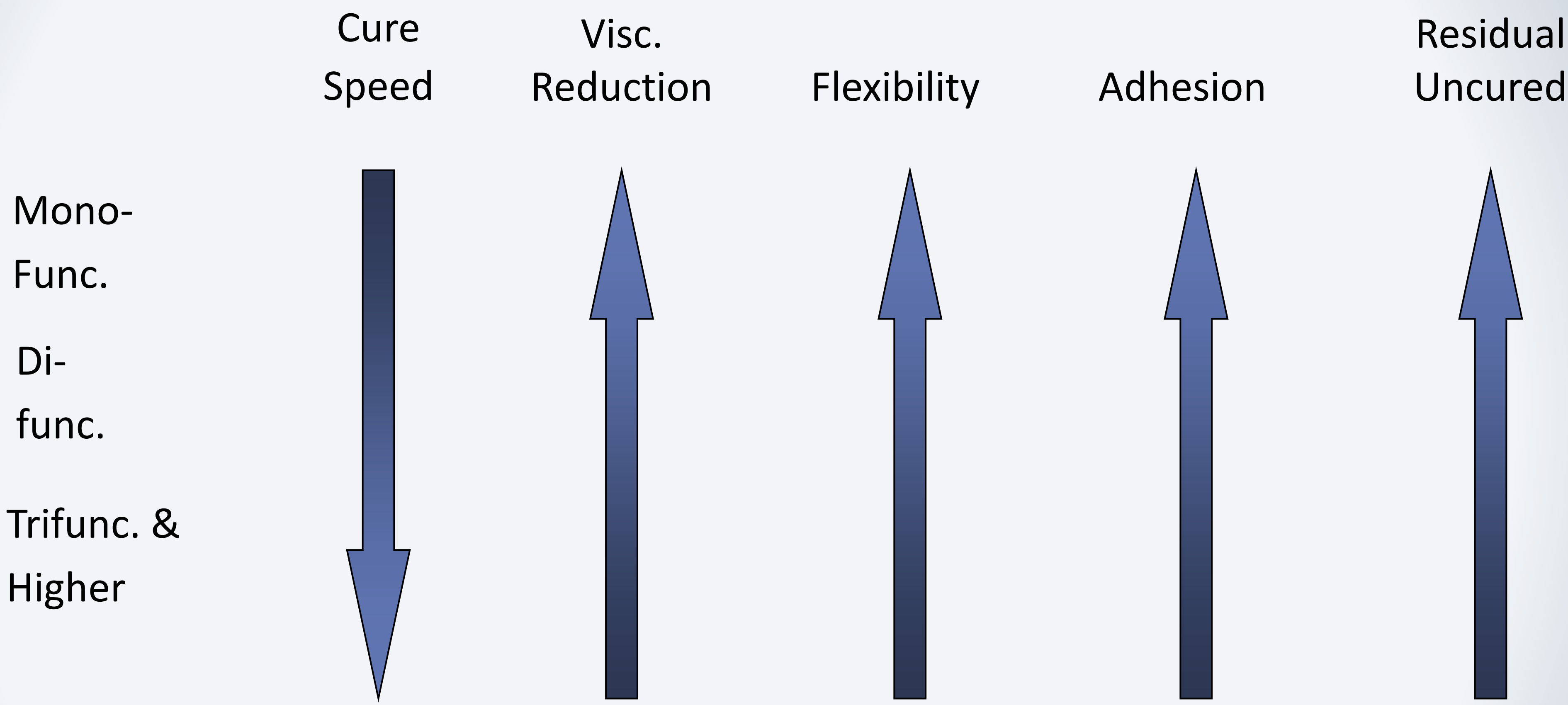
MONOMERS

Trifunctional Monomer



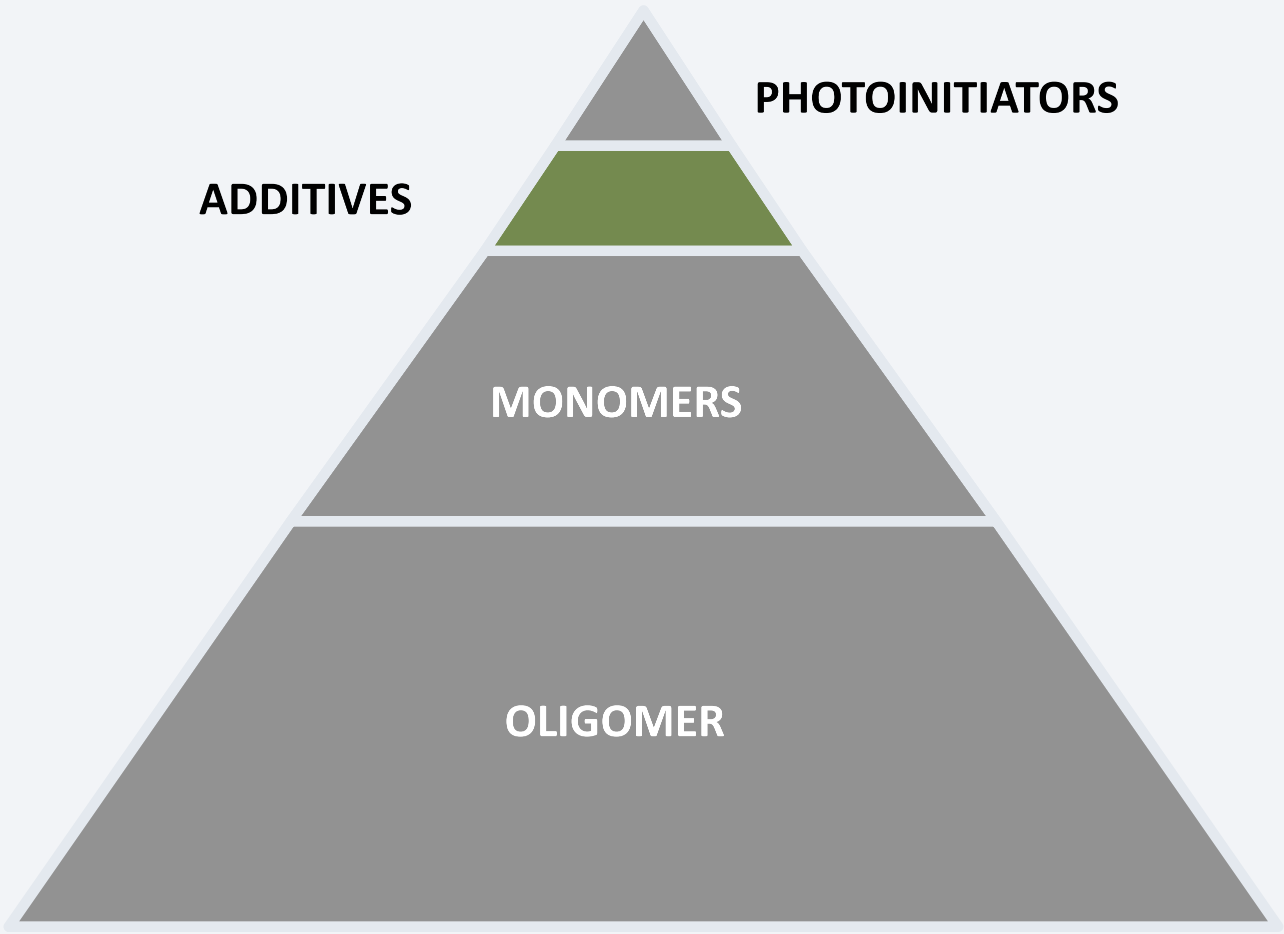
TMPTA
trimethylol propane triacrylate

Monomer Selection



Like all generalizations, these trends are usually, but not always, true

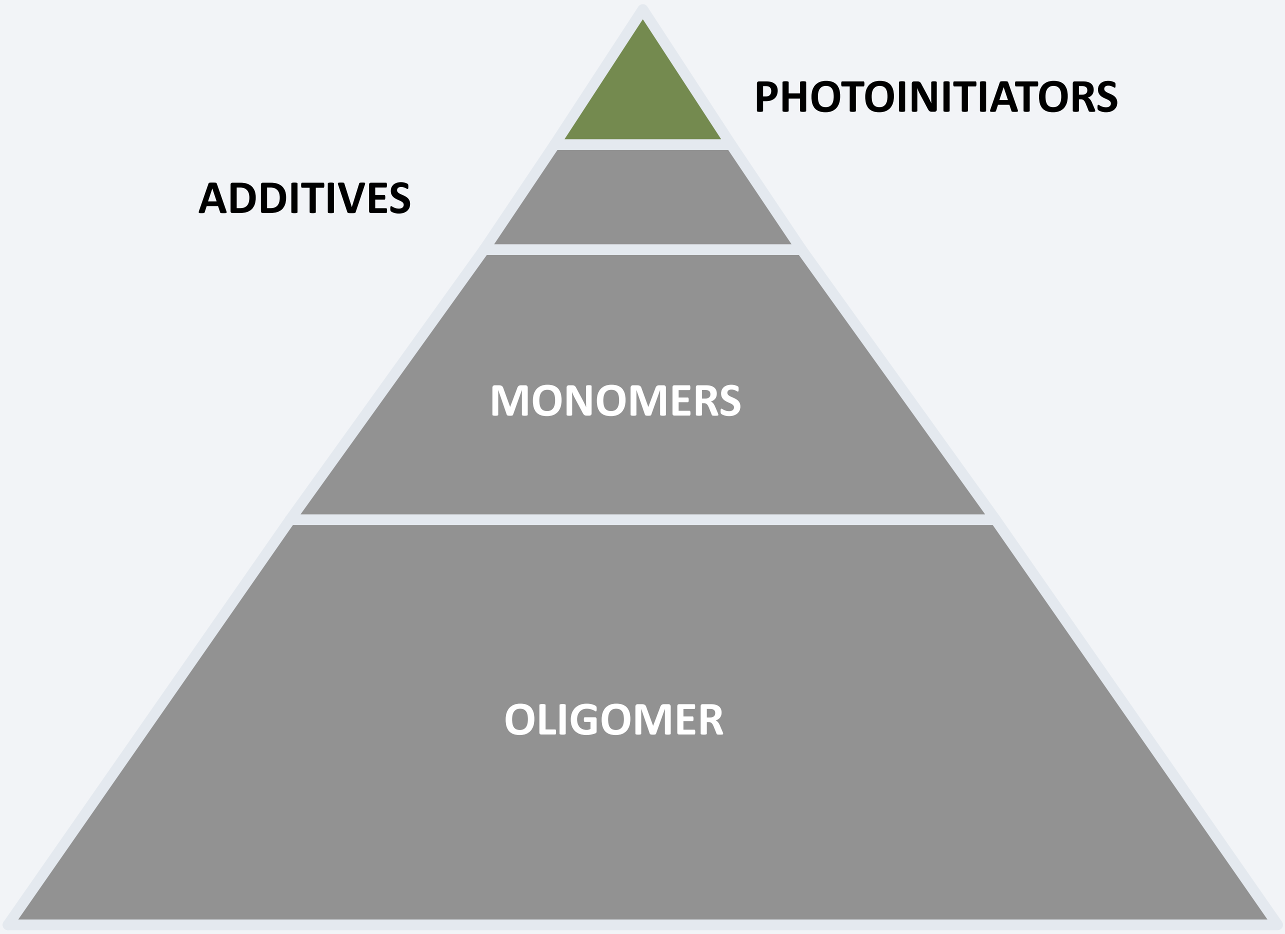
FORMULATING A UV CURABLE SYSTEM



ADDITIVES

- Pigments
- Fillers
- Defomers
- Flatting Agents
- Wetting Agents
- Slip Aids

FORMULATING A UV CURABLE SYSTEM



Photoinitiators

Terms/Glossary

λ_{max} (pronounced "lambda max")	The wavelength at which photoinitiator absorbs the most energy; also known as peak absorbance
absorbance	The amount of light a material takes in as opposed to reflecting or transmitting it
cure	The conversion of unreacted material to reacted material; transformation of monomers and oligomers to a polymer network; in practical terms, usually the point at which the wet material reaches a mar free state (or any other property of interest)
photons	A quantum of light; a packet of light energy
polymerization	The reaction by which monomers (and oligomers) are converted to high molecular weight materials (polymers)
radical	AKA free radical, molecule fragment with 1 unpaired electron. Not an ion (has no charge)
transmission	The amount of light passing through a material; the ratio between the outgoing (I) and the incoming intensity (I_o), $\%T = (I/I_o) \times 100$

Why Are PI Necessary?

- **PI Characteristics**
  - Absorb UV light or electrons to form active species (radicals or acids)
  - Add to monomer/oligomer to start cure process (polymerization)
  - Different PI absorb UV light at different wavelengths
  - Match PI λ_{max} with UV lamp output
  - Only reacts with UV-Vis energy, not heat
  - Long pot life/shelf life

UV Radical Polymerization

- Initiation
  - System is irradiated, reactive species (free radicals) created
- Propagation
  - Oligomers and monomers add to the growing polymer chain, creating a high MW network
- Termination
  - Two radicals combine to stop the chain reaction

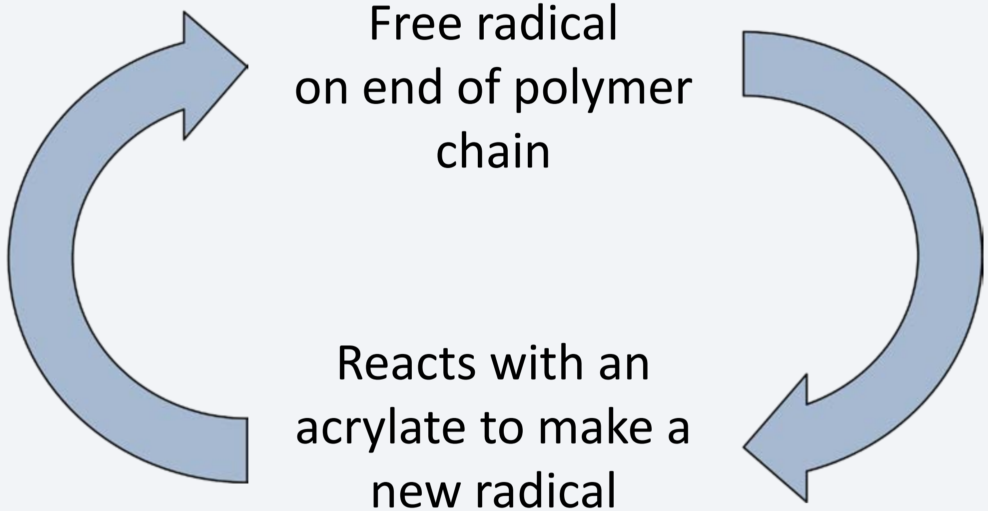
- Photoinitiators can be a factor in initiation and termination

Initiation

- **Initiation Process**
  - System is irradiated and the photoinitiator absorbs some of the incoming energy
  - Photoinitiator forms one or more free radicals
  - A free radical then combines with an acrylate to form a new radical that is the active species for the growing polymer
  - UV polymerization is line-of-sight only – shadowed areas very hard to cure

Propagation

- Propagation Process



- Referred to as a chain reaction

Termination

- **Termination Process**
  - Two radicals (active species, growing chains, PI fragments) combine and the polymerization stops
  - If PI concentration is too high, the radicals from the PI can contribute to a high termination rate
  - A high termination rate can lead to
    - Greater levels of unreacted material
    - Poor physical properties (e.g. low adhesion, greater marring, poor tensile properties)

Summary

- Initiation

$$I \xrightarrow{\text{UV Energy}} 2\,I\bullet$$

$$I\bullet + M \longrightarrow IM\bullet$$

- Propagation

$$IM\bullet + M \longrightarrow IMM\bullet$$

$$IMM\bullet + M \longrightarrow IMMM\bullet$$

$$IMMM\bullet + M \longrightarrow IMMMM\bullet$$

- Termination

$$P{\sim}M\bullet + \bullet M{\sim}P \longrightarrow P{\sim}M\text{-}M{\sim}P$$

-OR-

$$P{\sim}M\bullet + \bullet I \longrightarrow P{\sim}M\text{-}I$$

I = Initiator M = Monomer (or any acrylate) P = Polymer chain

Classes of Photoinitiators

- **Photocleavage (unimolecular PI)**

  a-cleavage PI - Adsorbs light and fragments to form the radicals which initiate polymerization.

- **Photoabstraction (bimolecular PI)**

  Hydrogen abstraction PI - Adsorbs light and abstracts hydrogen from another molecule (photoactivator) which produces radicals.

  Amine synergist (photoactivator) - Donates a hydrogen to the photosensitizer to produce the radicals which initiate polymerization.

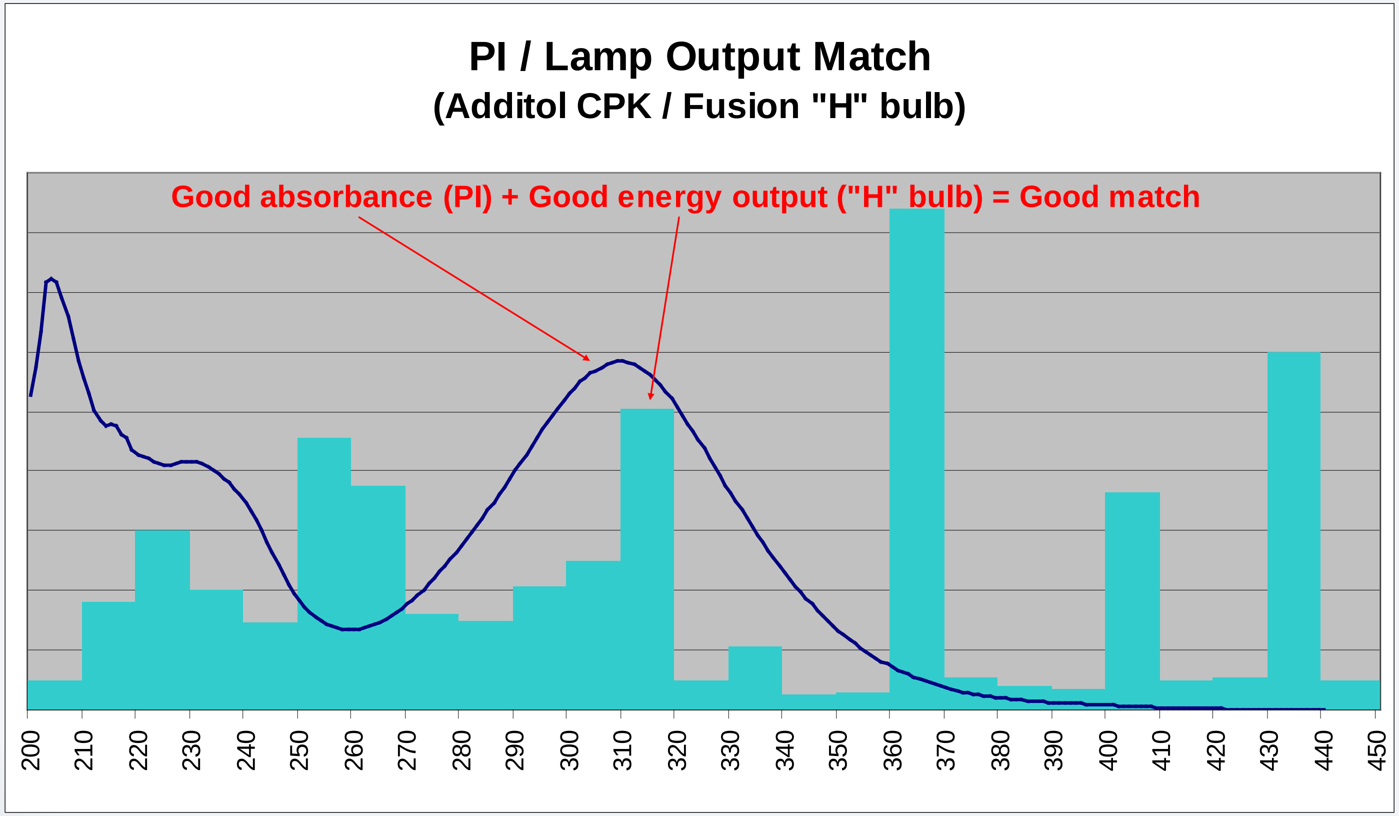
Photoinitiator, photosensitizer, and photoactivator are often used as different words for photoinitiators even though they are not the same

Photoinitiator Selection

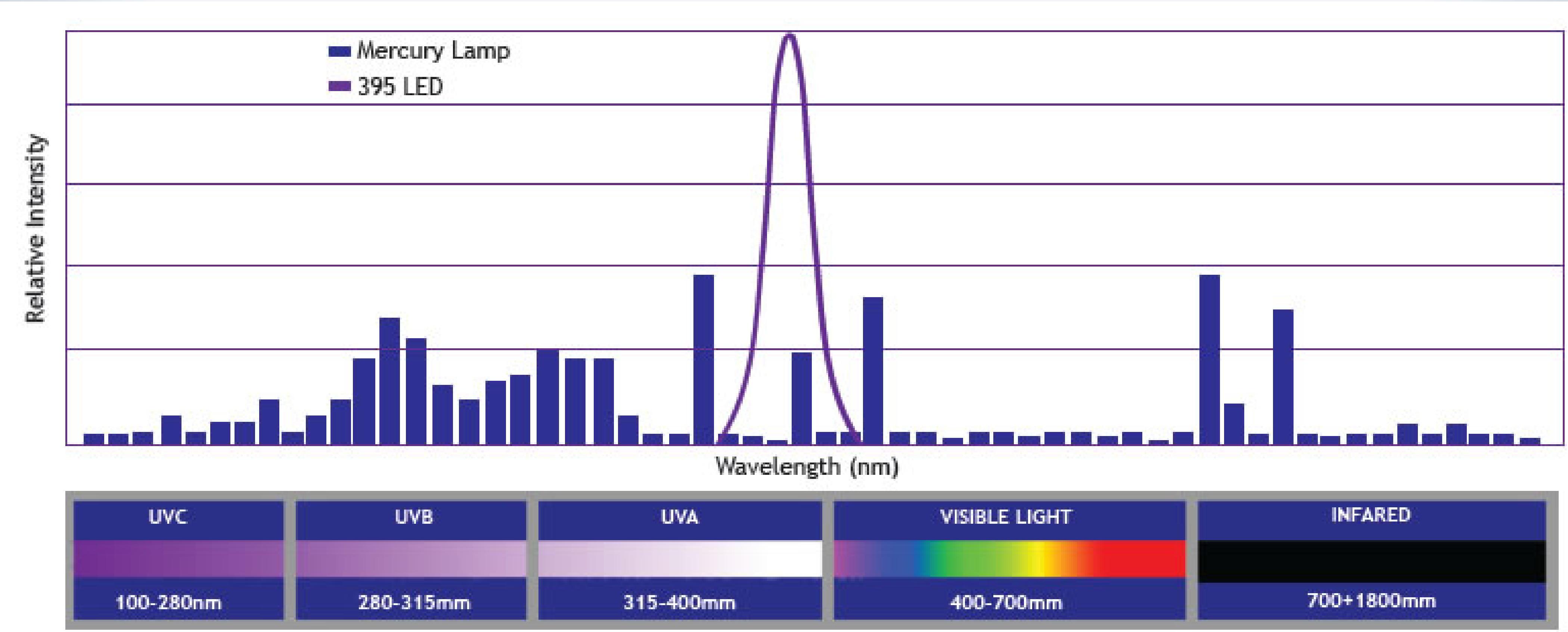
- Absorption characteristics of photoinitiator and formulated system
- Pigmentation
- Spectral output of UV lamps
- Oxygen inhibition
- Weatherability (yellowing)
- Handling (liquid vs. solid)
- Toxicity
- Cost

Matching PI with UV lamp

- Different UV lamps emit energy in different part of the spectrum
- Need to match absorbance of the PI with the output of the lamp for highest efficiency



UV-LED Output vs. Mercury Lamp



Oxygen inhibition

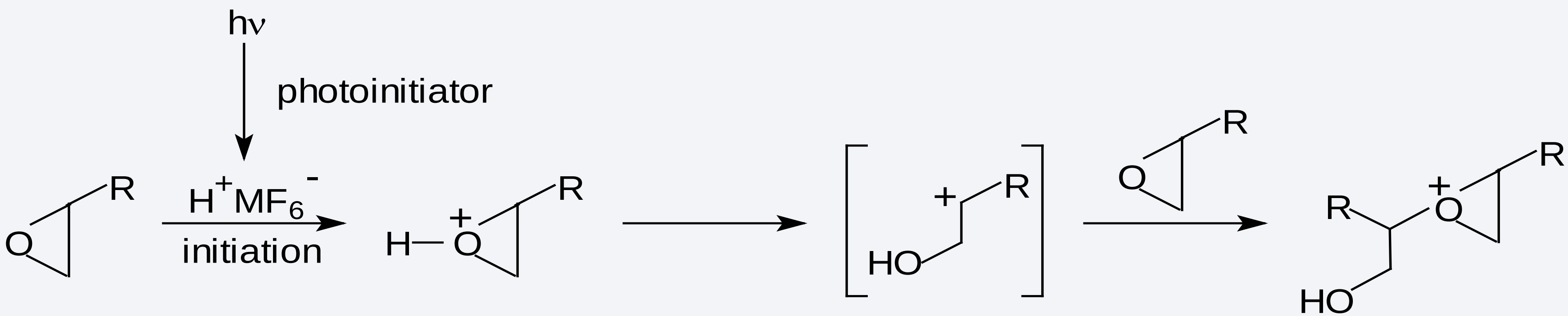
- Oxygen can inhibit (slow down) the cure speed of coatings and inks, especially in thin layers

- Solutions:
  - Cure under an inert (N2) atmosphere
  - Thiol-Enes
  - Cationic Chemistry
  - Amine synergists
  - Increase light intensity/duration (increase number of free radicals)

Cationic Cure

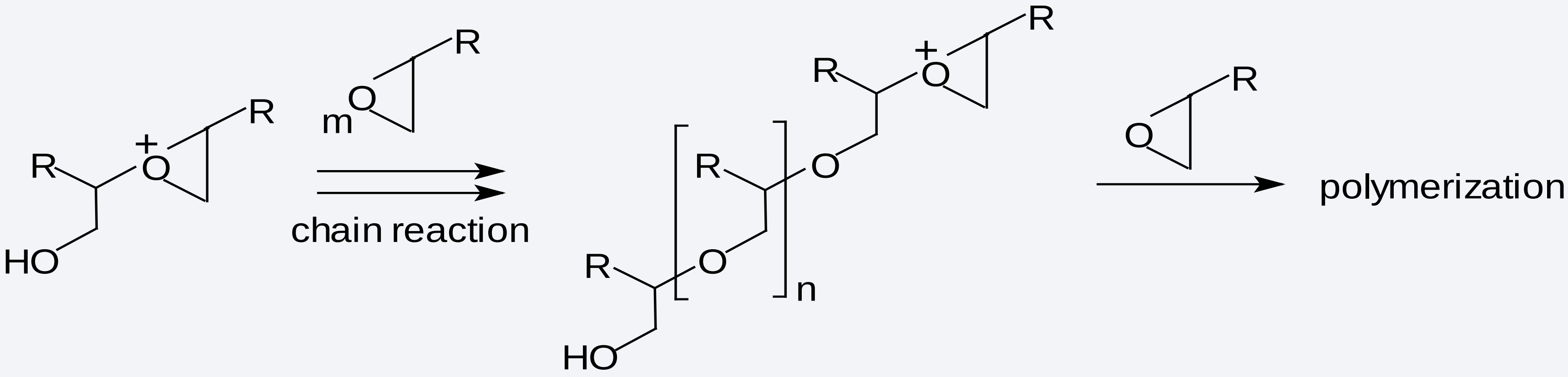
CATIONIC CURING MECHANISM

Initiation (Light & Heat)



CATIONIC CURING MECHANISM

Polymerization (Chain Reaction; Heat)



Radical vs. Cationic

Radical	Cationic
wide variety of raw materials	more limited raw materials
inhibited by oxygen	not inhibited by oxygen
not inhibited by high humidity	inhibited by high humidity
not inhibited by basic materials	inhibited by basic materials
full cure in seconds	full cure in hours
shrinkage - greater	shrinkage - less
adhesion - less	adhesion - greater
depth of cure - greater	depth of cure - less
cost - less	cost - greater
UV/EB market share - 92-94%	UV/EB market share - 6-8%

UV Cationic Curing

- **Cycloaliphatic Epoxide(s)**

  basic coating properties
- **Polyol(s)**

  crosslinking, flexibility
- **Epoxy/Vinyl Ether Monomer(s)**

  viscosity reduction
- **Additives**

  performance fine tuning
- **Photoinitiator Package**

  cation generation - commonly sulphonium salts

UV

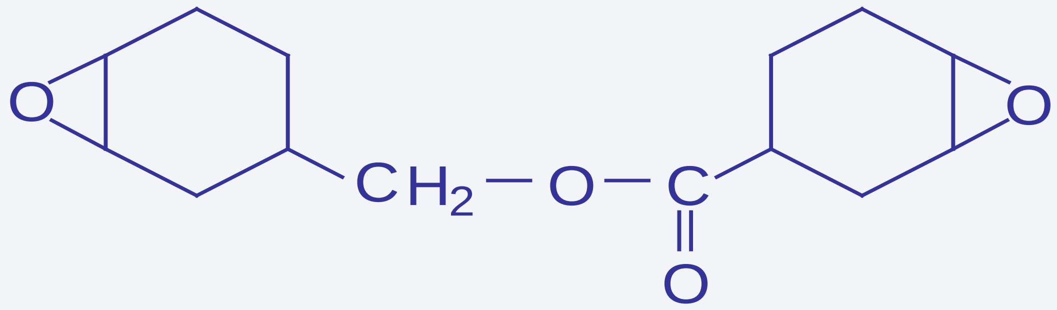
Light

CURED PRODUCT

Epoxides

Cycloaliphatic Epoxides

- Major Component of the formulation
- Builds properties of the film
- Other components are modifiers



Electron Beam

ELECTRON BEAM

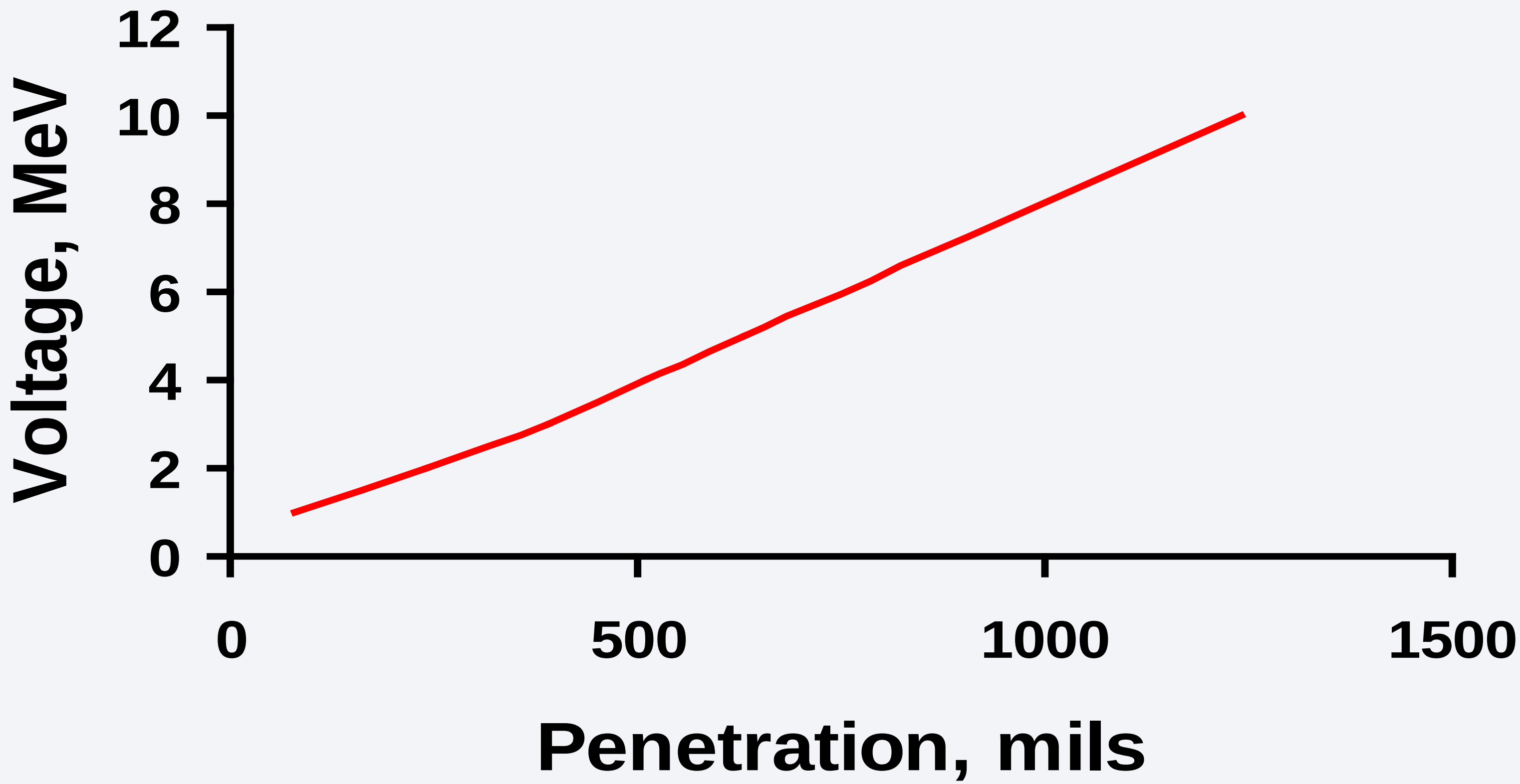
Ionizing radiation or low energy electrons (e^-)

- have sufficient energy to break bonds in coating, and generate free radicals
- can penetrate into and through a coating/ink, and through some substrates
- are not affected by pigmentation or transparency of coating/ink or substrate
- generate little to no heat
- dose can be precisely controlled
- enable high through put

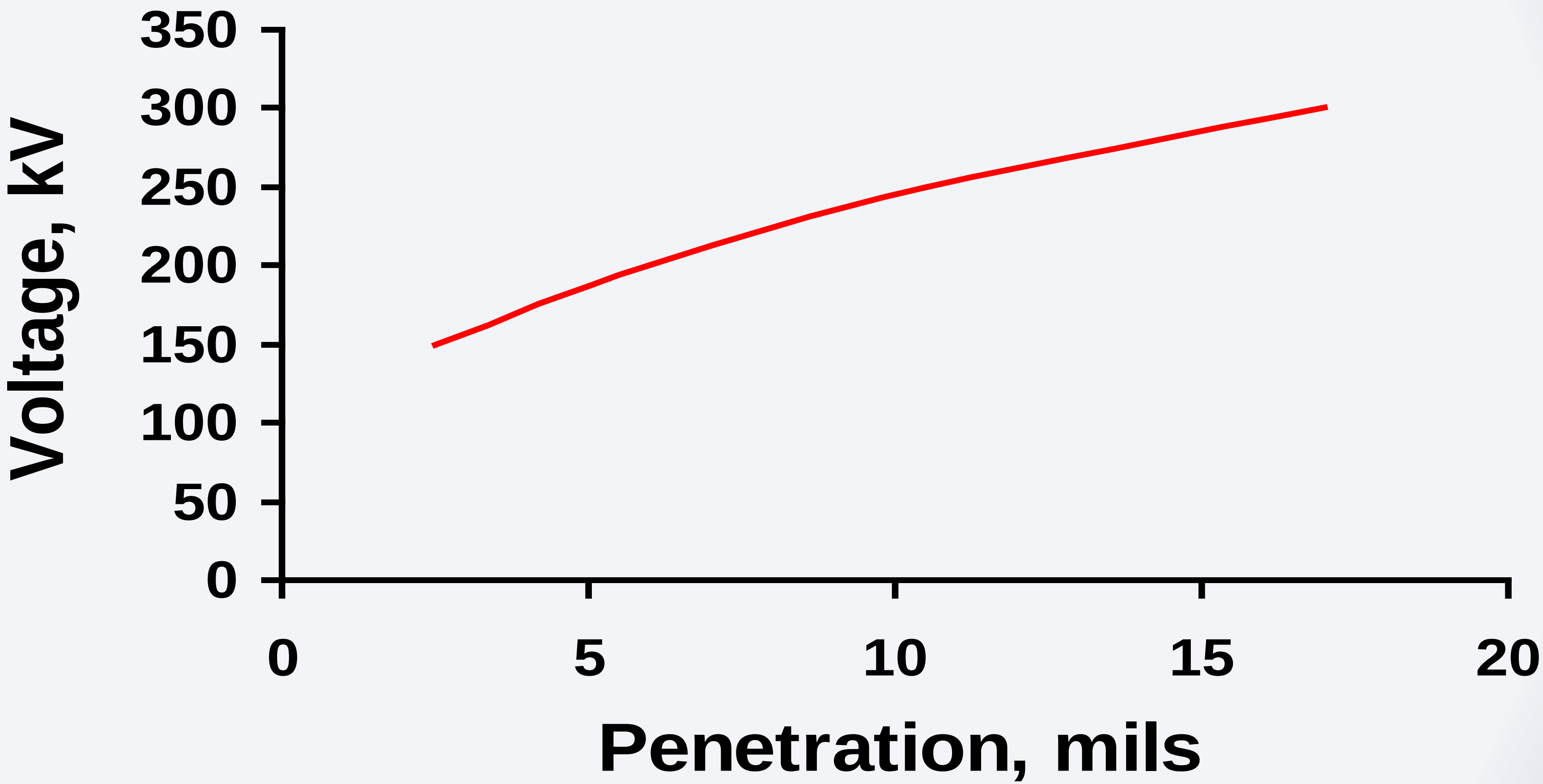
E BEAM PARAMETERS

- <u>Voltage</u> = Electron Penetration
  - Equals Thickness Penetrated
  - units are e^{-} volts: MeV, keV
- <u>Amperage</u> = Beam Current
  - Equals Exposure Intensity
  - units are amps
- <u>Dose</u> = Absorbed Energy
  - Expressed in kGy (kiloGray) or Mrad (mega rad)

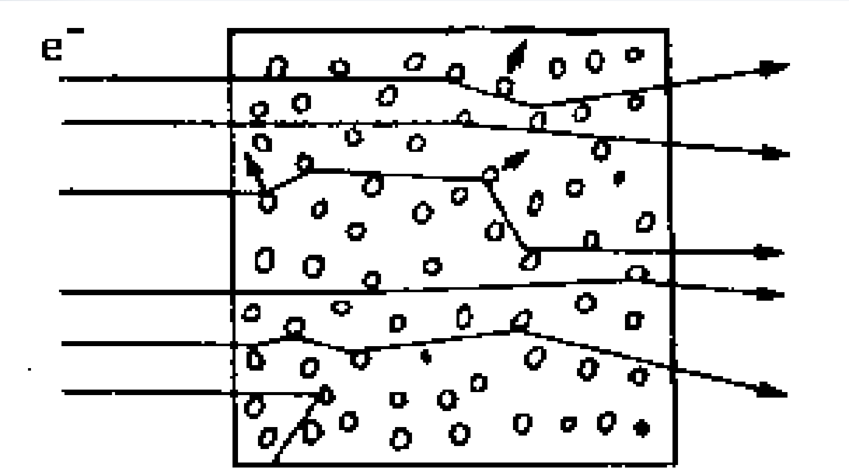
High Voltage E BEAM PENETRATION

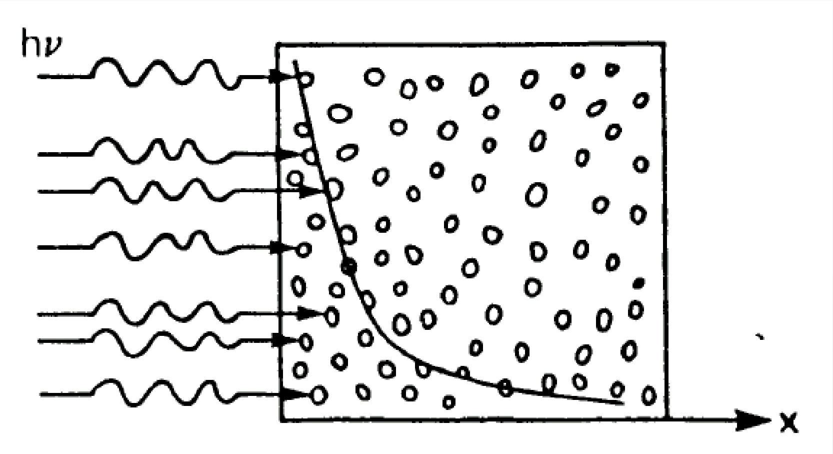


LOW VOLTAGE E BEAM PENETRATION

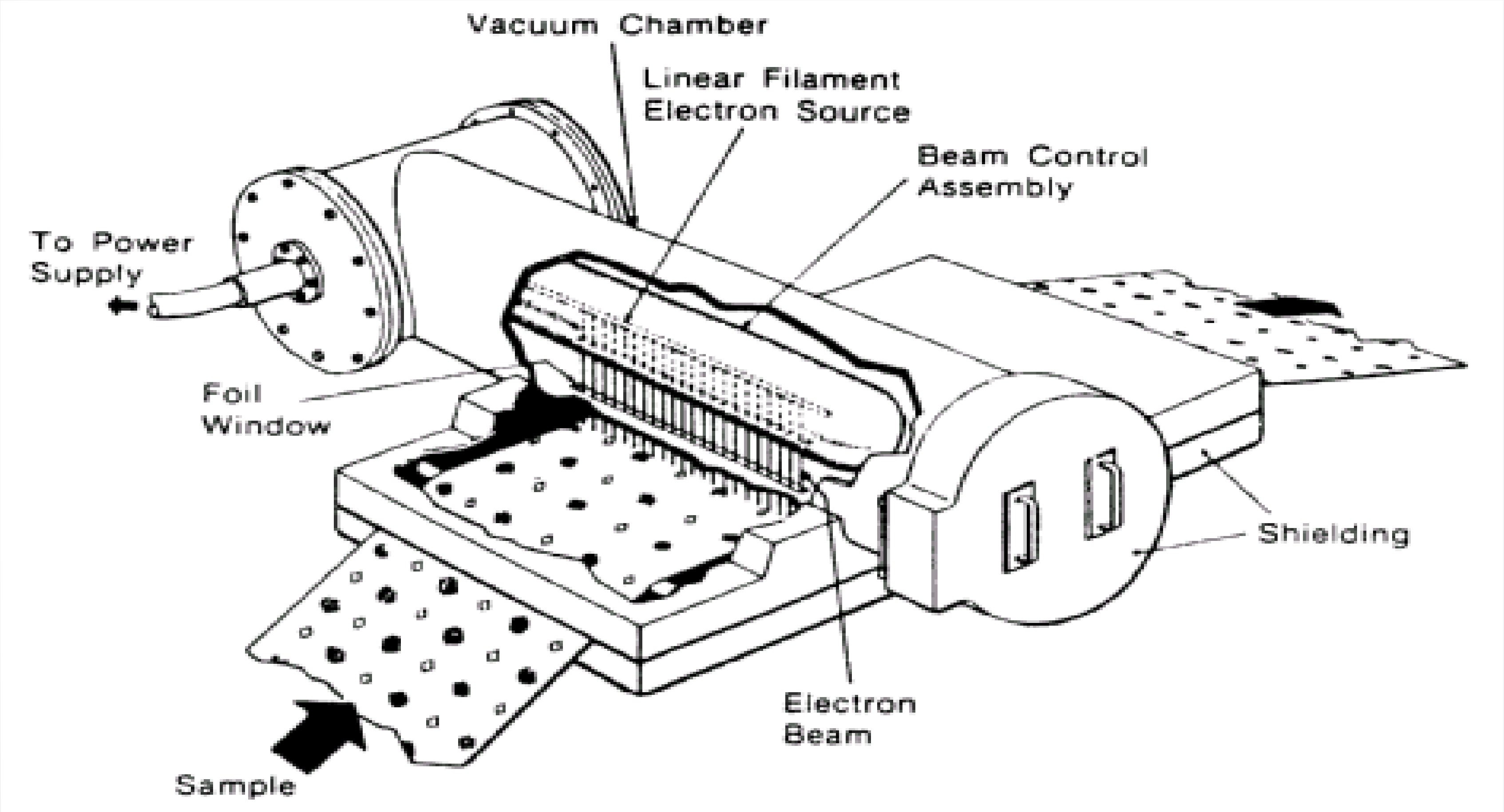


e^- AND hν PENETRATION





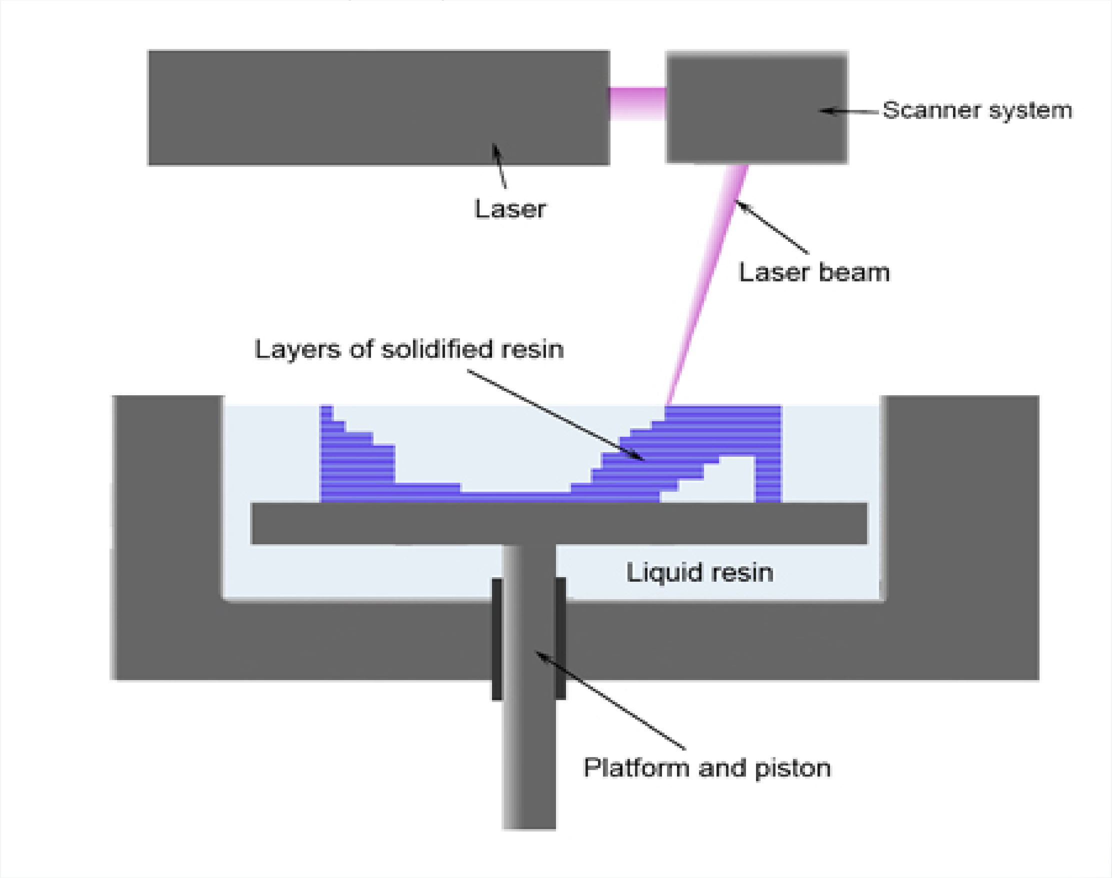
LOW VOLTAGE E BEAM



Basics in Action – UV Curable 3D Printing

3D Printing with UV - Types

- Stereolithography
  - A three-dimensional printing process that makes a solid object from a computer image by using a computer-controlled laser to draw the shape of the object onto the surface of liquid plastic.



3D Printing – Applying the Basics

- Conversion and Material Properties
- Viscosity/flow
  - Need to work with complex 3D objects
- Formulation basics
  - Monomers for flexibility, viscosity reduction
  - Oligomers for the key properties
- Photoinitiator matched to Lamps
  - UV Absorbers
- Oxygen Inhibition

The mechanism of Oxygen Inhibition

- Atmospheric oxygen exists typically in a highly reactive state
- In the polymerization initiation steps
  - Oxygen quenches or neutralizes the photoinitiator reactive states
  - Oxygen reacts with initiator radicals to form peroxy radicals
- In the main part of the polymerization
  - Oxygen reacts with polymer radicals to form peroxy radicals
- Characteristics of Peroxy radicals
  - Low reactivity compared to carbon radicals
  - Slows down cure

Oxygen Inhibition of Free Radical Cure

- Initiation

$$I \xrightarrow{\text{UV Energy}} 2\,I\bullet$$

$$I\bullet + M \longrightarrow IM\bullet$$

$$I\bullet + O_2 \longrightarrow I + O_2\bullet$$

$$IM\bullet + O_2\bullet \longrightarrow M\text{-}O\text{-}O\bullet$$

$$IM\bullet + M \longrightarrow IMM\bullet$$

$$IMM\bullet + M \longrightarrow IMMM\bullet$$

- Propagation

$$IMMM\bullet + M \longrightarrow IMMMM\bullet$$

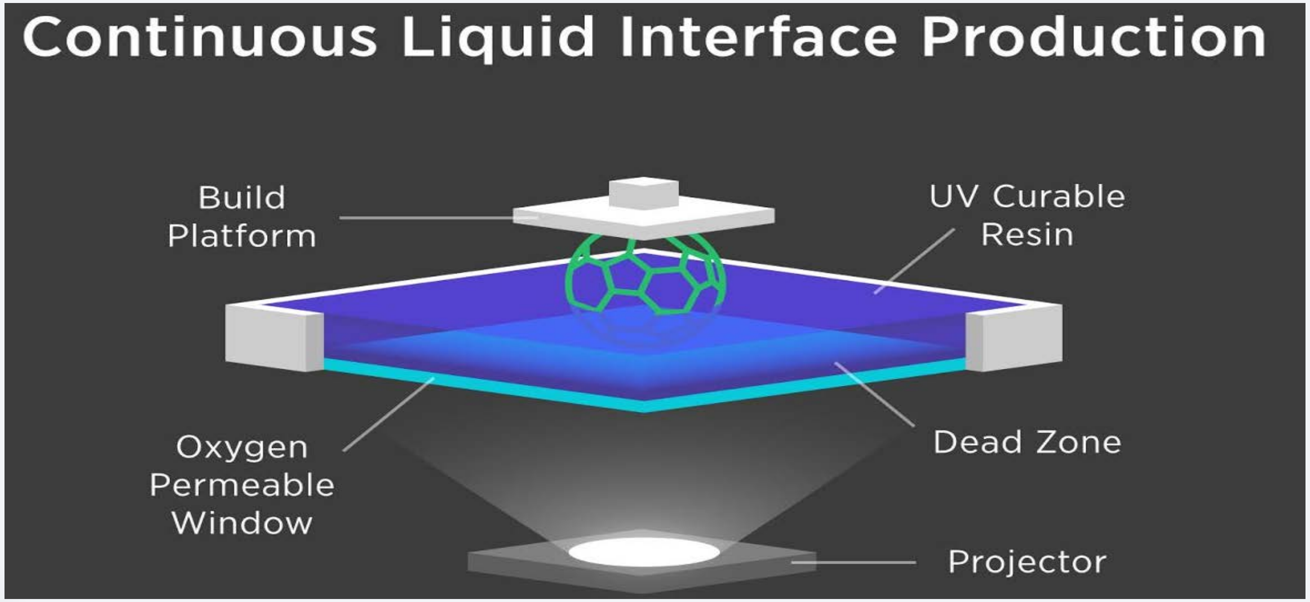
I = Initiator   M = Monomer (or any acrylate)   P = Polymer chain

What can be done about Oxygen Inhibition?

- Results of Oxygen Inhibition
  - Thin layer of unpolymerized molecules at the surface of the coating
  - Thickness of the unpolymerized layer is dependant on
    - Inverse of exposure time
    - Amount of light that the object sees (radiation intensity)
    - Photoinitiator concentration
- The cured part can be cleaned with an appropriate solvent such as isopropyl alcohol and then post cured by exposure to a UV lamp
- Ironically, oxygen inhibition could possibly be used to decrease the cure at the interface between the 3D object and the surface of the printer. This will minimize the adhesion of the object to the printer stage or tray.

O_2 Inhibition – Ally not the Enemy

- Carbon3D
- CLIP Technology - Continuous Liquid Interface Production
- By carefully balancing the interaction of light and oxygen, CLIP continuously grows objects from a pool of resin.
- http://carbon3d.com/



Thank You!

Dr. Mike J. Idacavage
Director of Business Development
Colorado Photopolymer Solutions
Email: mike.idacavage@cpspolymers.com
Phone: (303) 551-3213

Adjunct Associate Professor
Radiation Curing Program
SUNY-ESF